



## COVER SHEET

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**Non-destructive identification of As- and Co-minerals from Cobalt City,  
Ontario, Canada: Arsenolite, Erythrite and Sphero-cobaltite on  
(Para)Rammelsbergite**

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**Abstract**

A Ni-Co-As ore sample from Cobalt City, Ontario, Canada was examined with Scanning electron microscopy and Energy Dispersive X-ray analysis. In addition to cobaltian (para)rammelsbergite with variable cobalt content, for which Cobalt City is the type locality, and erythrite one new minerals was observed for this locality. Well formed crystals of arsenolite,  $\text{As}_2\text{O}_3$ , were found embedded in what appears to be fibrous sphero-cobaltite,  $\text{CoCO}_3$ . Additional information was obtained by Raman microscopy confirming the identification of the arsenolite. Both are considered to be secondary minerals formed by exposure to air resulting in oxidation and the formation of secondary carbonates.

**Keywords:** Arsenolite, pararammelsbergite, Raman microscopy, rammelsbergite, scanning electron microscopy, sphero-cobaltite

## Introduction

Pararammelsbergite is the low temperature polymorph of  $\text{NiAs}_2$  and has a similar paragenesis as rammelsbergite. The crystal structure of pararammelsbergite was described by Fleet <sup>1</sup>. Both minerals are well known from the arsenide and sulfarsenide assemblages in the Cobalt area, Ontario, Canada. It is actually the co-type locality for pararammelsbergite. The first descriptions go back to the thirties of the previous century (e.g. <sup>2-6</sup>). Jebrak <sup>7</sup> presented a review on the ore deposits of central Europe and Ontario in which he recognised 5 episodes. The general mineral formation sequence was quartz, uraninite-quartz, arsenides of Ni-Co and Ag (rammelsbergite, safflorite, dolomite-calcite), sulfides (pyrite, pyrrhotite, galena, chalcopyrite) with native Ag and carbonates (sometimes fluorite and barite) and late fillings by calcite. It is thought that the Ni-Co-Ag paragenesis, which is the topic of this study, is formed from alkaline, reducing, very saline fluids.

Arsenolite,  $\text{As}_2\text{O}_3$ , is commonly found as an oxidation product of other arsenic-bearing sulfides in hydrothermal veins in association with minerals such as claudetite, realgar, orpiment and erythrite. It crystallises as tiny octahedra sometimes with modifications by the dodecahedron. Spherochalcite,  $\text{CoCO}_3$ , is a member of the calcite group with a characteristic purplish colour, which is rather similar to that of erythrite although lighter. It has been observed as a rare accessory mineral in hydrothermal cobalt-bearing mineral deposits in association with minerals such as roselite, erythrite, annabergite, cobaltian calcite and cobaltian dolomite. Spherochalcite commonly forms radiated, concentric masses and crusts.

Presented here is a detailed non-destructive micro-analytical study of two new Co-As minerals, which have probably formed as secondary minerals, from the Cobalt area, Ontario, Canada. This paper intends to establish their nature and origin in relation to the original sulfidic ore minerals such as rammelsbergite and pararammelsbergite for which Cobalt is the type locality. Due to the very small nature of some of the secondary minerals commonly used techniques such as powder X-ray diffraction can not be applied. The chemical and morphological information obtained from Scanning Electron Microscopy is not sufficient in many cases to uniquely identify the nature of the minerals present in a sample. The use of Raman microscopy can add important structural information on each individual mineral phase, possibly resulting in a positive mineral identification. The ore sample studied in this paper is a good example of the combined strength of Scanning Electron Microscopy with Raman microscopy in the identification of the primary and secondary minerals present.

## **Sample**

The sample from Cobalt City, Ontario, Canada, owned by JTK, used in this study is a small, about 1 centimeter by 5 millimeter piece mainly consisting of a matrix of calcite and quartz covered by a number of ore minerals. The only two minerals that could be identified based on its optical properties were metallic silvery white (para)rammelsbergite and pink erythrite. Associated with it are small brownish crystals and purplish pink coloured areas. Since the sample is so small no analysis with X-ray diffraction could be performed. Therefore Scanning Electron Microscopy and Raman microscopy were used as alternative methods to identify the minerals present.

## **Experimental methods**

### *Scanning Electron Microscopy*

Scanning electron microscope (SEM) photos were obtained on a FEI QUANTA 200 Environmental Scanning Electron Microscope operating in this case at high vacuum and 20 kiloVolts (carbon coated sample) or 3 kiloVolts for the uncoated sample. This system is equipped with an Energy Dispersive X-ray spectrometer with a thin window capable of analysing all elements of the periodic table down to carbon. For the analysis a counting time of 100 seconds was applied.

### *Raman microscopy*

The sample was placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 reciprocal centimeters ( $\text{cm}^{-1}$ ) in the range between 100 and 4000  $\text{cm}^{-1}$ . 256 acquisitions using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5  $\text{cm}^{-1}$  line of a silicon wafer.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was

undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting, function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of  $r^2$  greater than 0.995.

## Results and Discussion

The surface of the sample is mainly covered by a metallic silvery massive coating. EDX analysis identified this as cobaltian (para)rammelsbergite (Fig. 1). The cobalt content is rather variable over the surface, as has been described before <sup>7, 8</sup>. The matrix is confirmed to consist mainly of quartz and calcite as already observed under the optical microscope. Intimately intergrown with the (para)rammelsbergite is erythrite,  $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  (Fig. 1). Additional confirmation was obtained from the Raman spectra as shown in Figure 2. In earlier work by Mrose *et al.* <sup>9</sup> the presence of cobaltian annabergite/erythrite was reported.

A second area of minerals was identified on the side and could be seen under the optical microscope as a mainly reddish brown and purplish area with small crystals on the surface. The small crystals on the surface show perfect octahedral morphology, sometimes slightly elongated along the a-axis. This indicates that this mineral belongs to the isometric or cubic crystal system (Figs. 3a, b). Also twins were observed formed according to a mirror plane perpendicular to the c-axis (Fig. 3c). Average

crystal size is about 10-20 nanometers. EDX analysis revealed only the presence of As and O leading to the identification of this mineral as arsenolite,  $\text{As}_2\text{O}_3$  (Fig. 3d). According to our extensive literature search this mineral only one publication has briefly described arsenolite from this locality<sup>9</sup>. The presence on the surface indicates that the arsenolite is formed as a secondary mineral compared to the massive (para)rammelsbergite, quartz and calcite, while it is embedded in second unidentified fibrous mineral. Arsenolite is thought to have formed as an oxidation product of primary arsenic ore minerals in for example hydrothermal veins. Confirmation of the identification as arsenolite can be obtained from the Raman spectra as shown in Figure 2. The spectrum is in complete agreement with that of both natural and synthetic arsenolite (Table 1)<sup>10, 11</sup>. The spectrum shows a medium intensity  $E_g$  mode at  $180\text{ cm}^{-1}$ . Two  $A_g$  modes are observed as a strong band at  $368\text{ cm}^{-1}$  and a medium strong band at  $560\text{ cm}^{-1}$ . The  $T_{2g}$  modes are all observed as weak bands at 265,, 413, 469 and  $781\text{ cm}^{-1}$ .

The fibrous mineral's crystal size is much smaller than that of the arsenolite and has a very high aspect ratio (Fig 4). Initial EDX analysis indicated the presence of a high amount of Co in addition to O and C, but there was a lot of interference from the underlying crystals making a good quality chemical analysis impossible. Therefore the accelerating voltage of the SEM was turned down from 20 kV to 3 kV thereby enhancing not only the surface signal due to a lower penetration depth of the electron beam but also because the high energy transitions of the heavier elements like Si, Ni and As are no longer observed. The resulting spectrum shows a high amount of C and O in addition to the Co signal which is still present. This indicates that the fibrous mineral must be a form of cobalt carbonate, possibly spherocobaltite  $\text{CoCO}_3$ . The

long needle-like habit can be explained by its hexagonal crystal structure with a strong elongation along the c-axis. A clean Raman spectrum could not be obtained (Fig. 2b) but carbonate bands around 727 and 1437  $\text{cm}^{-1}$  can only be interpreted as being the  $\nu_4$  and  $\nu_3$  modes, similar to that of calcite that has the same crystal structure<sup>12</sup>. White<sup>13</sup> reported infrared bands at 869, 1485 and 747  $\text{cm}^{-1}$  for spherocobaltite (cobaltcalcite). A weak band was observed at 268  $\text{cm}^{-1}$ , which has an equivalent band at 279  $\text{cm}^{-1}$  for calcite<sup>10</sup>. The remainder of the spectrum is associated with underlying erythrite (see Fig. 2b for comparison with synthetic erythrite).

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TABLE 1. PEAK ASSIGNMENT FOR THE STRONGEST BANDS IN THE RAMAN SPECTRUM OF ARSENOLITE.

Observed This study (cm <sup>-1</sup> )	Synthetic arsenolite <sup>11</sup> (cm <sup>-1</sup> )	Assignment <sup>11</sup>
180	184	$E_g$
265	268	$T_{2g}$
368	370	$A_{1g}$
413	415	$T_{2g}$
469	472	$T_{2g}$
560	561	$A_{1g}$
781	781	$T_{2g}$

## Figure captions

Fig. 1 a) SEM image and b) EDX spectrum of cobaltian (para)rammelsbergite

Fig. 2 Raman spectra of a) arsenolite and b) mixture of erythrite and spherocobaltite in comparison to synthetic erythrite <sup>14</sup>.

Fig. 3 SEM images of a) and b) well crystallised arsenolite with fibrous spherocobaltite, c) arsenolite twinning and d) EDX spectrum of arsenolite.

Fig. 4 a) SEM image of fibrous spherocobaltite with arsenolite crystals on the surface and b) EDX analysis at 3 kV.

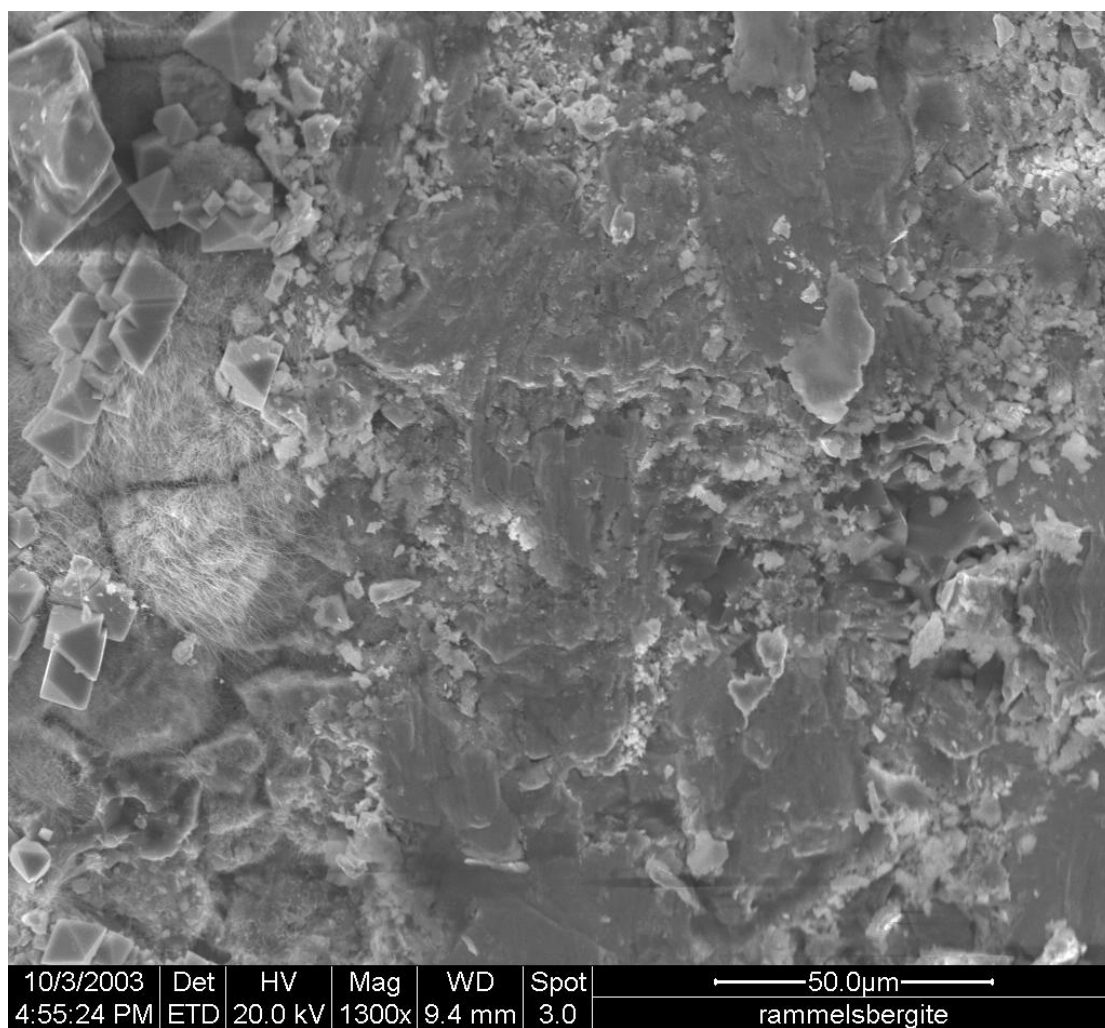


Fig. 1a

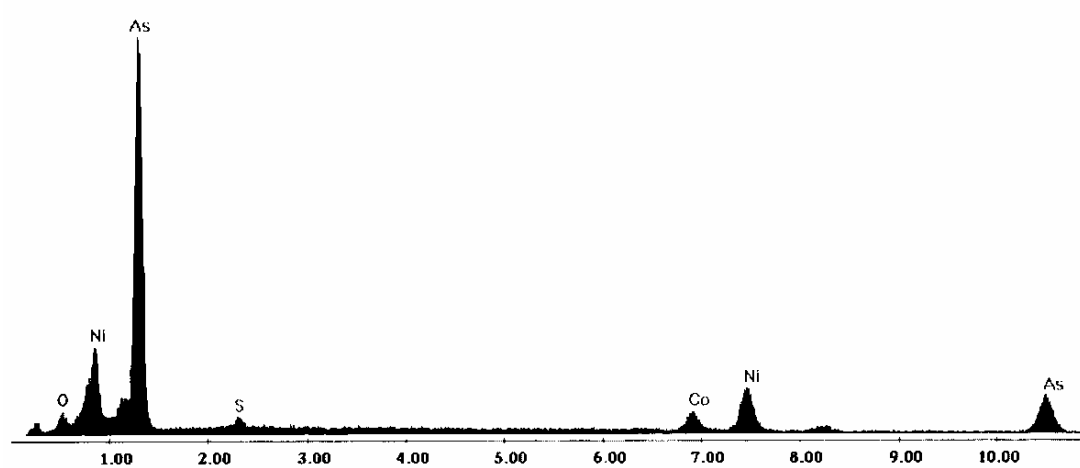


Fig. 1b

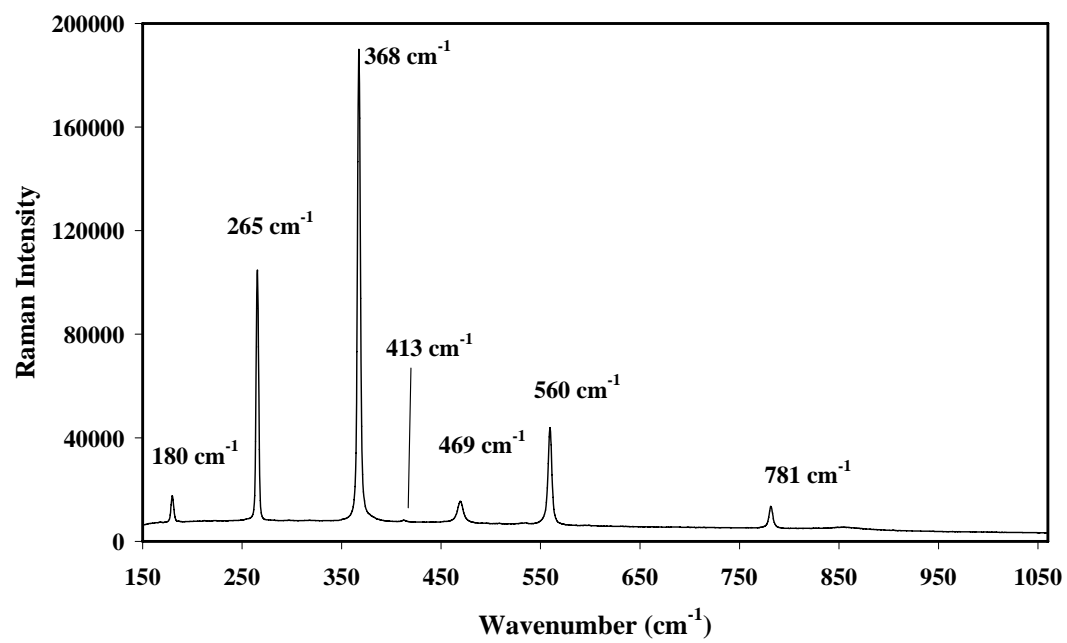


Fig. 2a

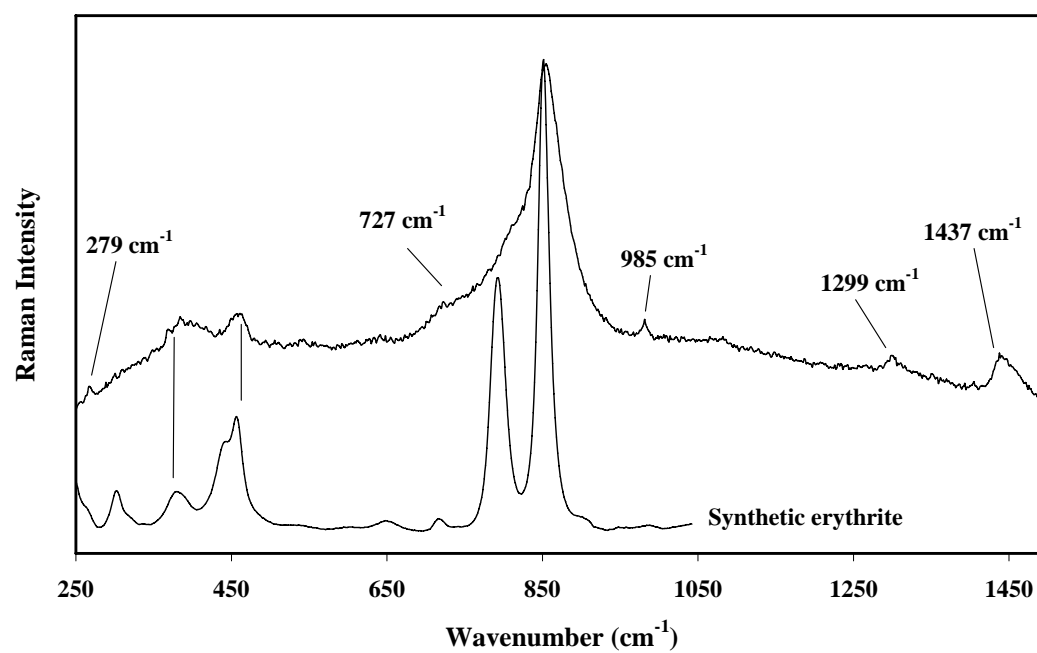


Fig. 2b

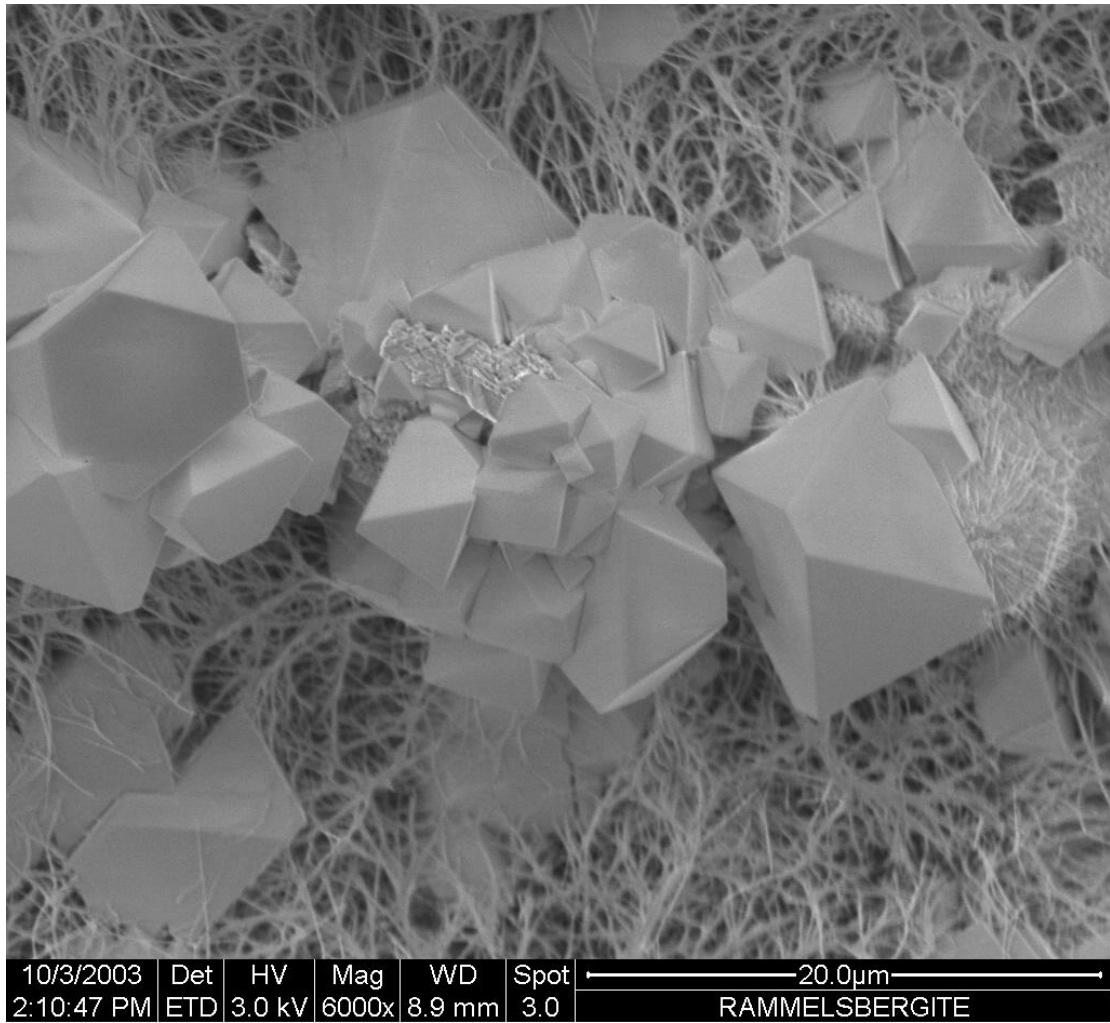


Fig. 3a

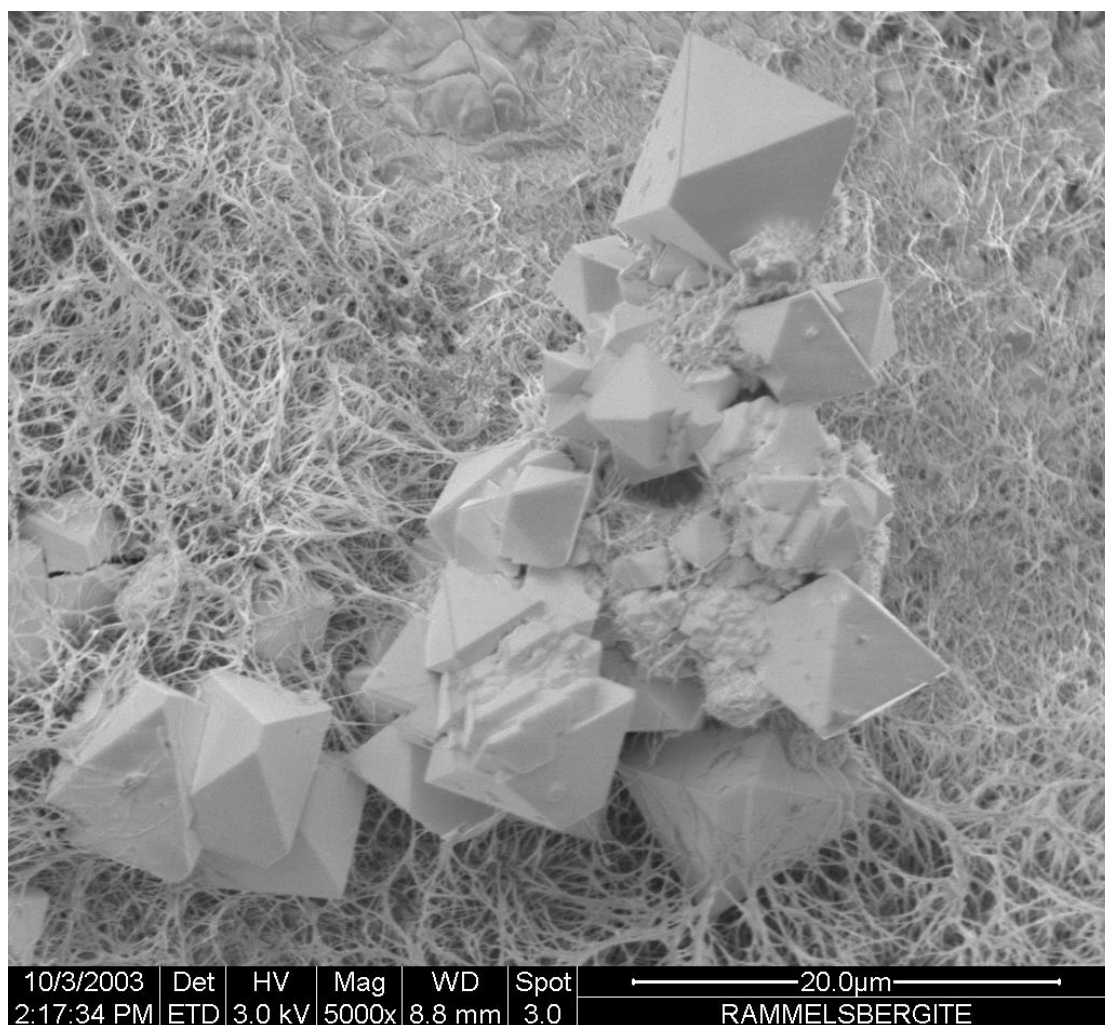


Fig. 3b

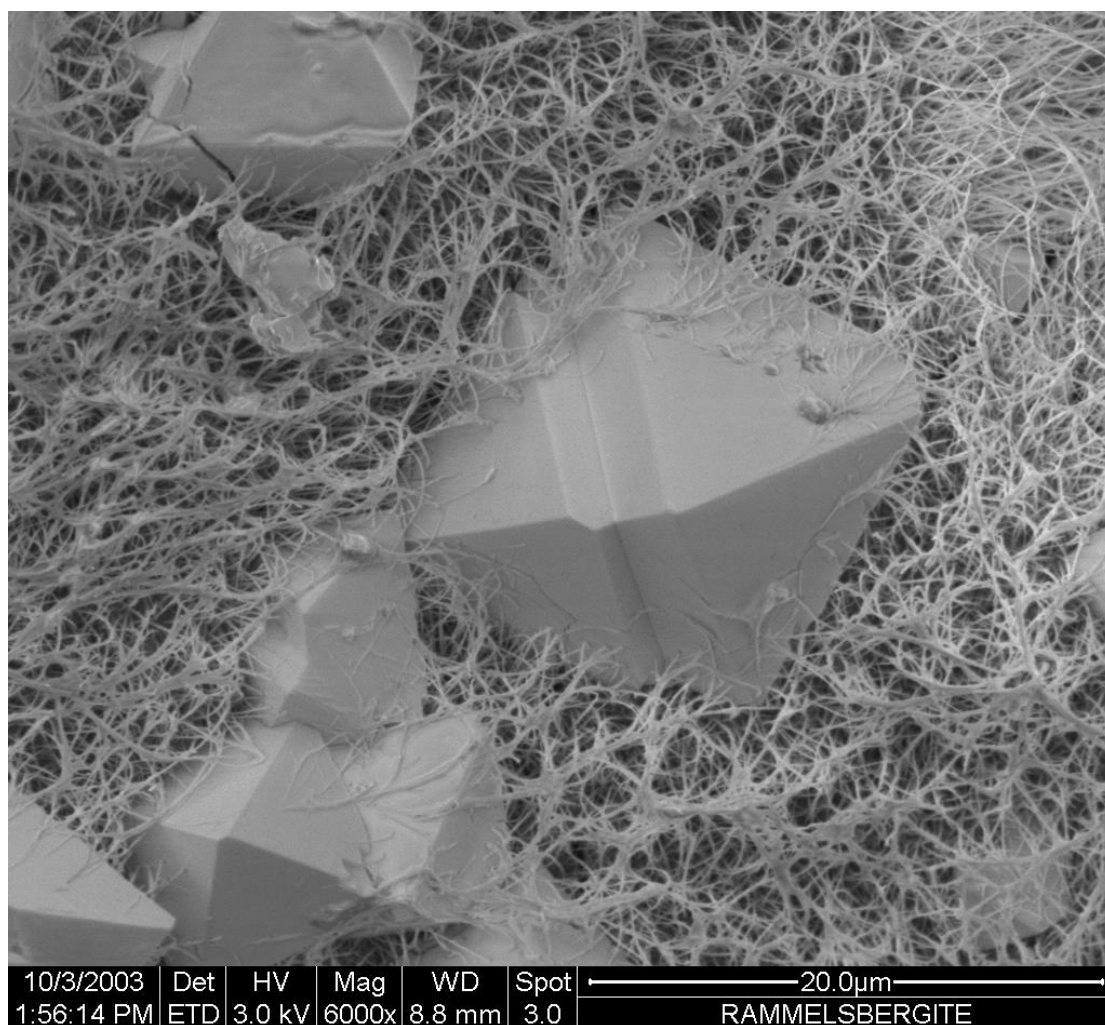


Fig. 3c

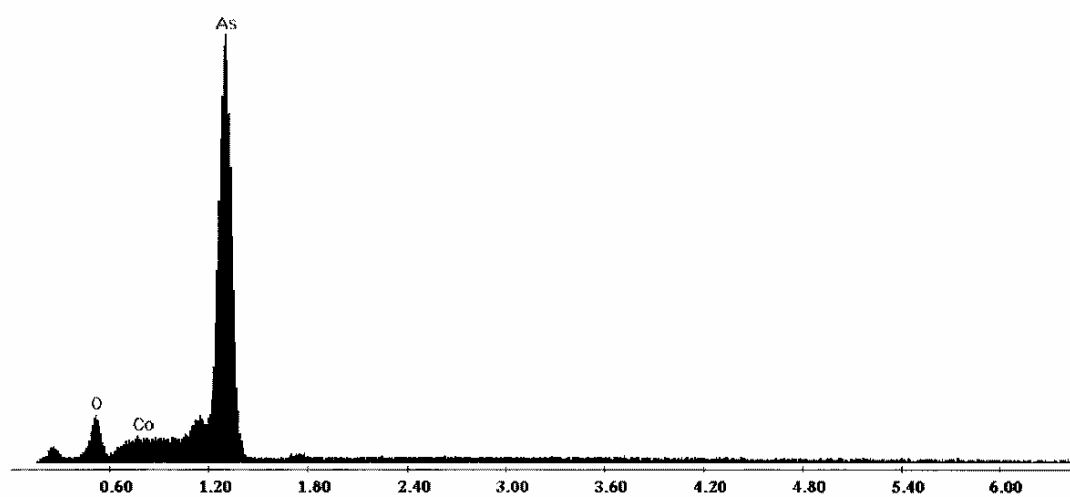


Fig. 3d



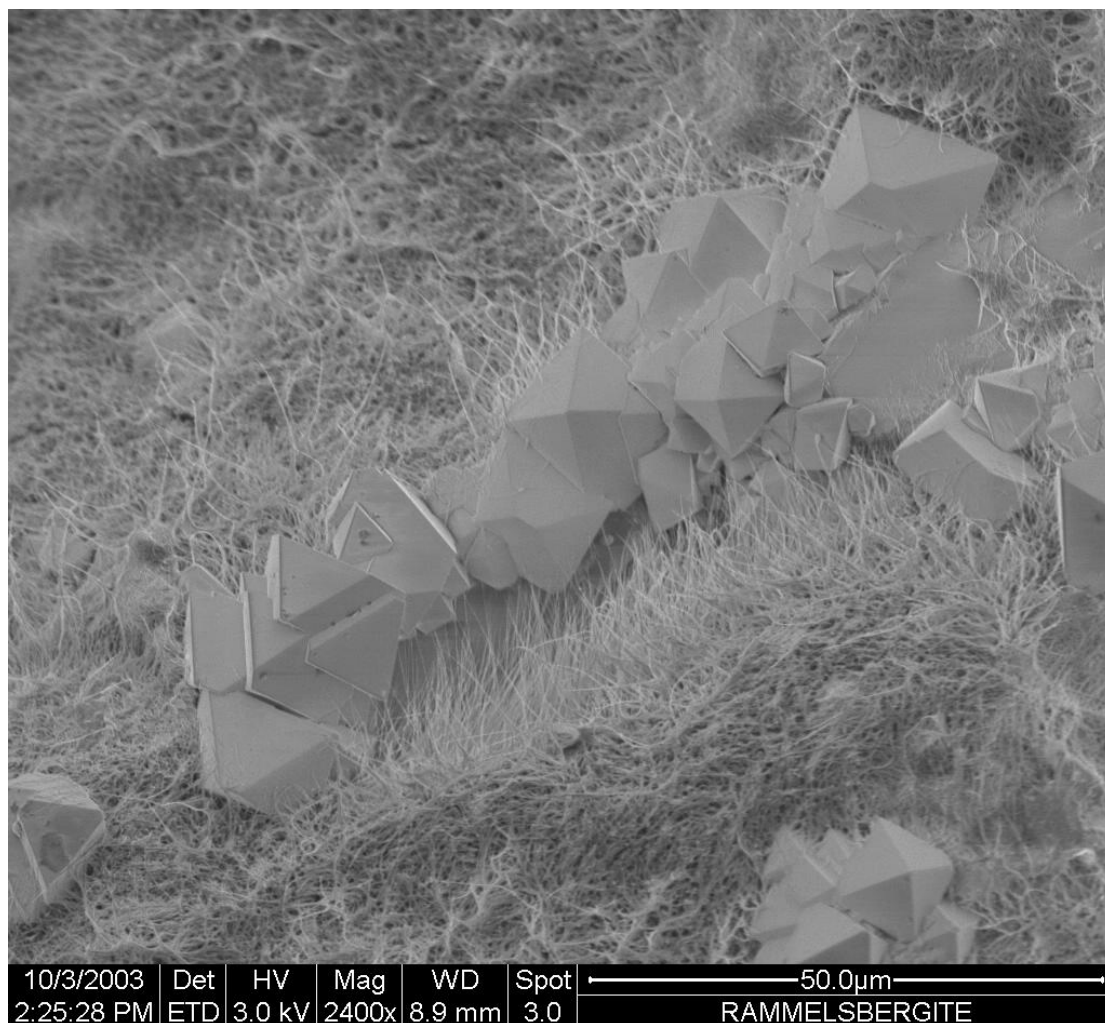


Fig. 4a

